

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE STANDARD OIL CO. (IND.)]

Experimental Equilibrium Constants for the Isomeric Hexanes

By B. L. EVERING AND E. L. D'OUVILLE

In the course of the development of the naphtha isomerization process^{1,2} the equilibrium constants for the isomeric hexanes were determined. Although the equilibrium constants for butanes and pentanes^{3,4} have been repeatedly investigated, few experimental data have appeared for the hexanes. Two papers^{5,6} have appeared on the direct experimental determination of the equilibrium constants for the hexanes but they were limited to 25 and 80°, respectively. The hexane equilibria were calculated over a wide range of temperatures from the precise measurements of the heats of combustion and best available entropy data.⁷ In the present investigation the hexane equilibria were studied directly over the temperature range 21 to 204° and side reactions were reduced to a minimum by the use of hydrogen and cyclic decomposition inhibitors. The experiments were carried out on a fraction of Mid-Continent light naphtha containing both C₅ and C₆ hydrocarbons.

All experiments were made in a stirring reactor wherein efficient contact was obtained between the catalyst and the reactants.

Experimental Method

A batch type stirring apparatus consisting of a 1490-cc. capacity carbon steel reactor (Fig. 1) was employed throughout this investigation. The reactor was heated with steam or hot oil by circulating these materials through a jacket surrounding the reactor. The reactor could be brought to reaction temperature in five minutes with steam and in half an hour with the hot circulating oil. In the case of steam the reactor could be quenched in five minutes by circulating cold tap water through the surrounding jacket. Cooling was somewhat slower with the hot oil since cold water could not be circulated through the jacket to cool the reactor.

The reactor was mechanically stirred at 1725 r. p. m. by a one-half horsepower electric motor driving a ³/₈ inch steel shaft operating through a double packing gland, the details of which are shown in Fig. 1. The lower packing holds the reactor pressure and any leakage past the main packing gland is measured by a gas meter attached to the vent between the lower and upper packing glands. In actual service, no difficulty has been experienced with leakage up to pressures of 5000 lb./sq. in. Successful operation depends primarily on the use of a drill rod shaft in conjunction with an asbestos type packing impregnated with a heavy oil and water cooling of the packing glands. The reactants were agitated with a 2.5 inch three bladed up-thrust propeller placed near the bottom of the reactor. A bleedout tube dipped to near the bottom of the reactor so that liquid product could be withdrawn. The reactor system was equipped with the necessary accessory equipment to measure in known amounts of anhydrous hydrogen chloride from a calibrated pressure vessel by pressure drop and was also equipped for the addition of hydrogen.

An experiment was made as follows. Seventy-two grams of anhydrous aluminum chloride or its equivalent as aluminum chloride-hydrocarbon complex was placed in the reactor usually with one liter of light naphtha and promptly sealed. Twenty-two grams of hydrogen chloride was measured into the reactor as an activator. Hydrogen was added in the higher temperature runs until the total reactor pressure was 600 lb./sq. in. at room temperature. In the case of the experiments at 21°, anhydrous aluminum bromide, which is soluble in paraffins, was used as the catalyst in an effort to establish equilibrium more rapidly.

The reactor was heated to reaction temperature with stirring and sufficient time allowed for equilibrium to be established. At the end of this time the stirrer was stopped, the reactor was rapidly cooled and one-half hour allowed for settling the catalyst from the products. (It was experimentally established that no isomerization occurred during this cooling and settling period.) The liquid product was withdrawn from the reactor into a flask, the volatile products passed overhead through a soda lime tube to remove hydrogen chloride, then to a Dry Ice-acetone "knock back" to condense light hydrocarbons and finally to a wet test meter to measure the effluent hydrogen and any other non-condensable gases.

The products were distilled in a low-temperature column packed with glass helices equivalent to 20 theoretical plates to separate between butanes and lighter and the liquid product. Motor method octane numbers (CFR-ASTM D-357) were obtained on the liquid product for rapid estimation of the establishment of equilibrium. Those samples which had attained equilibrium were carefully fractionated in a wire gauze packed column testing 60—80

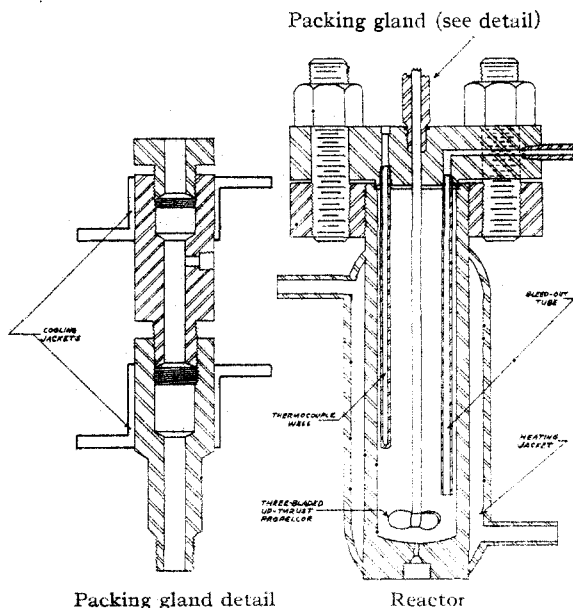


Fig. 1.

- (1) B. L. Evering, N. Fragen and G. S. Weems, *Chem. Eng. News* **22**, 1898 (1944).
- (2) J. E. Swearingen, R. D. Geckler and C. W. Nysewander, *Trans. A. I. Ch. E.*, **42**, 573 (1946).
- (3) Egloff, Hulla and Komarewsky, "Isomerization of Pure Hydrocarbons," Chapter I, Reinhold Publishing Co., New York, N. Y., 1942.
- (4) H. Pines, B. Kvetinskas, L. S. Kassel and V. N. Ipatieff, *THIS JOURNAL*, **67**, 631 (1945).
- (5) H. Koch and H. Richter, *Ber.*, **77**, 127 (1944).
- (6) G. C. A. Schuit, H. Hoog and J. Verheus, *Rec. trav. chim.*, **59**, 793 (1940).
- (7) F. D. Rossini and co-authors, API Research Project 44, "Selected Values of Properties of Hydrocarbons," Circular of the National Bureau of Standards C461, November, 1947.

theoretical plates. The accuracy of the analyses attainable with this column is shown in Table I by the fractional analysis of a known synthetic sample. The largest discrepancy from the true composition of the hexanes is in the determination of 2,3-dimethylbutane as it must be determined primarily from the refractive index and this is partially obscured by the high index of cyclopentane. Mass spectrometer analyses (not available when the analyses were made) have invariably shown the concentration of 2,3-dimethylbutane determined by fractional analysis to be approximately 20% low; therefore the values reported for 2,3-dimethylbutane in this investigation have been corrected upward by this amount with an accompanying decrease in the value of 2-methylpentane.

TABLE I

ACCURACY OF FRACTIONAL ANALYSES OF HEXANE ISOMERS

	Volume, %	
	Actual composition	Fractionation
Cyclopentane	3.8	4.0
2,2-Dimethylbutane	20.8	19.7
2,3-Dimethylbutane	7.9	6.2
2-Methylpentane	30.6	34.3
3-Methylpentane	15.8	15.7
<i>n</i> -Hexane	14.2	12.2
Methylcyclopentane	5.4	7.0
Benzene	1.5	0.9

Materials.—The aluminum chloride was a product of the Hooker Electrochemical Company. The anhydrous hydrogen chloride was from the Harshaw Chemical Company and was guaranteed 96% pure. Hydrogen was Linde commercial grade and was used from cylinders without further purification.

The hydrocarbon used in this investigation was a 67° end-point cut of Mid-Continent naphtha containing 0.009 weight per cent. sulfur and having the composition shown in Table II. Although the hydrocarbon feed contained considerable amounts of material other than hexanes in the form of pentanes, naphthenes and a small amount of aromatics, they are not believed to have any detrimental effect on the equilibrium of the hexanes. In fact, the naphthenes and benzene serve the useful function of being decomposition inhibitors, thus reducing side reactions.

TABLE II

COMPOSITION OF MID-CONTINENT LIGHT NAPHTHA (67° End-point)

	Volume, %
Isopentane	1.5
<i>n</i> -Pentane	35.9
Cyclopentane	3.0
2,2-Dimethylbutane	1.0
2,3-Dimethylbutane	1.0
2-Methylpentane	23.3
3-Methylpentane	13.4
<i>n</i> -Hexane	17.4
C ₆ Naphthenes	3.0
Benzene	0.5

Experimental Results

For accurate equilibrium data the first problem is assurance of the establishment of complete chemical equilibrium and the second is the reduction to a minimum of all side reactions that might affect this equilibrium.

In order to avoid the time-consuming fractional analysis of the products from all the experiments,

a rapid method of determining the approach to and establishment of equilibrium was used. Since the octane numbers⁸ of hydrocarbons increase with increase in the branching, determination of the octane number of the product gave a rapid estimate of the extent to which the isomerization had progressed. Series of experiments made at increasing reaction time are plotted against octane number and the leveling off of the octane number curve indicated the establishment of chemical equilibrium. Only those experiments for which chemical equilibrium was established, were analyzed by fractional distillation. Figure 2 shows that equilibrium is established quite rapidly at 161° and very slowly at the lower temperatures and especially at 21°.

The side reactions accompanying isomerization at 21 and 161° are shown in Fig. 2 where the percentage of butane and lighter (condensables) formed are taken as a measure of decomposition and plotted against time. Side reactions increase rapidly with increase in temperature so that at 161° and above hydrogen pressure was used to inhibit decomposition. Since hydrogen pressure has a slight suppression effect on the rate of isomerization it was not used at 102° and lower where the isomerization rate is very slow; instead, advantage was taken of the decomposition-inhibiting action of the naphthenes and benzene contained in the light naphtha. The inhibiting of side reactions accompanying isomerization will be reported in more detail in a subsequent paper.

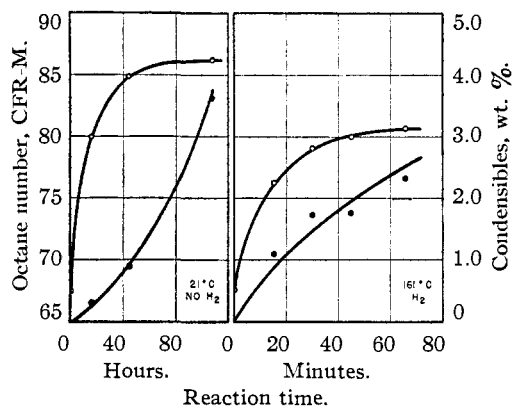


Fig. 2.—○—, CFR-M; —●—, decomposition.

Side reactions can have a pronounced effect on chemical equilibrium and lead to erroneous results⁹ due to the relative instability of one isomer compared to another and an unfavorable isomerization rate for the formation of the unstable isomer as it is depleted. For the equilibrium experiments at 21 and 161° the decomposition is sufficiently low that no appreciable error can be produced. Furthermore, although the decomposition curves in Fig. 2 are not linear, they do not indicate any

(8) J. Smittenberg, H. Hoog, B. H. Moerbeek and M. J. v. d. Zijden, *J. Inst. Petroleum*, **26**, 294 (1940).

(9) J. R. Bates, *THIS JOURNAL*, **68**, 511 (1946).

appreciable preferential decomposition of the more highly branched isomers as they are formed. At 102 and 204° the decomposition is considerably higher (Table IV) but does not lead to displacement of equilibrium. This was confirmed by isomerizing 2,3-dimethylbutane under insufficient hydrogen pressure so that a large amount of decomposition was produced and comparing with the results from an experiment in which the decomposition was substantially inhibited. The results reported in Table III indicate no significant difference for the two extreme cases.

TABLE III

Hydrocarbon	HEXANE EQUILIBRIUM	
	2,3-Dimethylbutane	2,3-Dimethylbutane
Cyclopentane, vol., %	8.3	0.0
AlCl ₃ , g.	69.0	73.6
HCl, g.	20.5	20.5
Contact time, min.	10	10
Temperature, °F.	320	313
H ₂ pressure, p. s. i.	550	550
Vol. % decomposition to lighter than C ₆	7.4	62.9
Analyses of hexanes, vol., %		
2,2-Dimethylbutane	22.6	21.8
2,3-Dimethylbutane	8.8	11.0
2-Methylpentane	37.3	35.2
3-Methylpentane	18.3	17.8
<i>n</i> -Hexane	13.0	14.2

TABLE IV

Temperature, °C.	COMPOSITION OF REACTOR CONTENTS AT EQUILIBRIUM			
	21	102	161	204
Moles				
Hydrogen	0.785	0.900
Hydrogen chloride	0.310 ^a	0.356	.493	.246
Propane	.010	.055	.020	.121
Isobutane	.360	.920	.382	.714
<i>n</i> -Butane	.044	.324	.232	.223
Isopentane	2.600	2.325	2.515	1.841
<i>n</i> -Pentane	0.463	0.414	0.815	0.768
Cyclopentane	0.209	0.300	.271	.131
2,2-Dimethylbutane	2.295	1.400	.936	.538
2,3-Dimethylbutane	0.386	0.367	.346	.220
2-Methylpentane	.879	1.005	1.341	.928
3-Methylpentane	.342	0.477	0.671	.440
<i>n</i> -Hexane	.167	.336	.419	.349
Methylcyclopentane	.035	.173	.278	.200
Cyclohexane	.573	.352	.272	.120
Vapor/liquid ratio (at reactor temp.)	Liquid	.006	.75	Vapor
Mole % decompn.	5.0	15.3	7.4	15.9

^a Anhydrous hydrogen bromide.

Hexane Equilibria.—Table IV shows the results of experiments at 21, 102, 161 and 204° in which equilibrium had been established. Since the contents of the reactor were cooled to room temperature before removal, the analyses reported in Table IV are for the combination of vapor and liquid phases which existed at reaction condi-

tions. The true equilibrium values for the hexanes in the vapor and liquid phases were calculated from these data by finding the vapor and liquid composition that existed in the reactor at the experimental temperature and pressure. This was solved by trial and error knowing the fugacities of the various components in the system. The fugacities of the components in the reactor at experimental conditions were obtained from compressibility charts¹⁰ using the best published vapor pressures and critical constants appearing in the literature. The physical properties of the isomeric hexanes were taken from the work of Willingham, Taylor, Pignocco and Rossini¹¹ for temperatures below the boiling point and from the work of Kay¹² at higher temperatures. The fugacities for hydrogen and hydrogen chloride are based on unpublished data from this Laboratory. The vapor and liquid phase equilibrium values for the isomeric hexanes are given in Table V together with the phase or vapor-liquid ratio calculated as existing at experimental conditions.

At 21° the phase is known to be entirely liquid and at 102° the vapor-liquid ratio can be calculated quite accurately. However, at 161°, which is relatively close to the critical and 204° which is just above the critical, the exact phase or vapor-liquid ratio cannot be known with great certainty. This uncertainty in the vapor-liquid ratio at the two higher temperatures cannot lead to any substantial errors as calculations assuming the found analyses to be either entirely vapor or entirely liquid are quite close at 161° and are equal at the critical. The composition limits for the several temperatures investigated are shown in Table V.

The vapor phase equilibrium values for the isomeric hexanes from the last column of Table V are plotted in Fig. 3. These values are compared with those obtained from the entropies and heats of combustion⁷ and the experimental values of Koch and Richter⁵ at 25° and Schuit, Hoog and Verheus⁶ at 80°.

The agreement between the present values and those from the entropies and heats of combustion are good for *n*-hexane and 2,3-dimethylbutane but are in disagreement on 2,2-dimethylbutane and the methylpentanes. The temperature coefficient for all the isomers is in good agreement but the entropies and heats of combustion predict substantially more 2,2-dimethylbutane than has been found experimentally. Assuming that the difference lies entirely in the 2,2-dimethylbutane, then the discrepancy in the methylpentanes vanishes. Aside from the absolute values there is good agreement in the ratio of 2-methylpentane to 3-methylpentane.

The experimental equilibria determined for the hexanes by Koch and Richter⁵ at 25° are in ex-

(10) Weber, "Thermodynamics for Chemical Engineers," John Wiley and Sons, New York, N. Y., 1939, p. 198.

(11) C. B. Willingham, W. J. Taylor, J. M. Pignocco and F. D. Rossini, *J. Research Natl. Bur. Standards*, **35**, 219 (1945).

(12) W. B. Kay, *THIS JOURNAL*, **68**, 1336 (1946).

TABLE V
 EQUILIBRIUM COMPOSITION OF THE ISOMERIC HEXANES

Run	Composition	Temp., °C.	Reactor pressure, lb./sq. in. (gage)	Vapor- liquid ratio	Observed analysis, mole %	Composition limits		Equilibrium	
						Vapor, ^a mole %	Liquid, ^b mole %	Liquid, mole %	Vapor, mole %
1	2,2-Dimethylbutane	21	50	Liquid	56.4	66.4	45.6	56.4	66.4
	2,3-Dimethylbutane				9.5	8.2	10.5	9.5	8.2
	2-Methylpentane				21.6	16.9	26.3	21.6	16.9
	3-Methylpentane				8.4	6.0	11.2	8.4	6.0
	<i>n</i> -Hexane				4.1	2.5	6.4	4.1	2.5
2	2,2-Dimethylbutane	102	220	0.006	39.1	45.0	33.3	39.1	45.0
	2,3-Dimethylbutane				10.2	9.8	10.5	10.2	9.8
	2-Methylpentane				28.0	26.3	29.4	28.0	26.3
	3-Methylpentane				13.3	11.7	14.9	13.3	11.7
	<i>n</i> -Hexane				9.4	7.2	11.9	9.4	7.2
3	2,2-Dimethylbutane	161	875	0.75	25.2	26.2	24.1	24.9	25.9
	2,3-Dimethylbutane				9.3	9.9	8.8	9.1	9.7
	2-Methylpentane				36.1	35.2	37.0	36.4	35.5
	3-Methylpentane				18.1	17.6	18.6	18.2	17.8
	<i>n</i> -Hexane				11.3	11.1	11.5	11.4	11.1
4	2,2-Dimethylbutane	204	1080	Vapor	21.7	20.9	22.5		21.7
	2,3-Dimethylbutane				8.9	9.1	8.7		8.9
	2-Methylpentane				37.5	37.4	37.6		37.5
	3-Methylpentane				17.8	18.2	17.3		17.8
	<i>n</i> -Hexane				14.1	14.4	13.9		14.1

^a If observed analysis is all liquid. ^b If observed analysis is all vapor.

 TABLE VI
 COMPARISON OF $\Delta F/T$ FROM EXPERIMENTAL DATA WITH THE VALUES OF ROSSINI AND CO-AUTHORS

	25°C.		$\Delta F/T$ cal./deg. mole 127°C.		200°C.	
	This work	Rossini and co-authors	This work	Rossini and co-authors	This work	Rossini and co-authors
<i>n</i> -Hexane	0	0	0	0	0	0
2-Methylpentane	-3.68	-3.89	-2.39	-2.48	-2.06	-1.78
3-Methylpentane	-1.68	-1.88	-0.85	-1.00	-0.67	-0.60
2,3-Dimethylbutane	-2.23	-3.35	-0.22	-1.18	+0.79	-0.26
2,2-Dimethylbutane	-6.33	-7.98	-2.94	-4.30	-0.61	-2.60

cellent agreement with the present experimental values and lend support to the lower experimental values for 2,2-dimethylbutane over the higher values calculated by Rossini and co-authors.⁷ The values of Schuit, Hoog and Verheus,⁶ at 80° cannot be compared to the present values since no distinction was made between 2,2-dimethylbutane and 2,3-dimethylbutane and the total of the dimethylbutanes is obviously far from equilibrium. Their values agree well with the present values in the case of *n*-hexane and in the ratio of 2-methylpentane to 3-methylpentane.

The values of $\Delta F/T$ for the isomerization of *n*-hexane to the various isomers were calculated from the experimental equilibrium constants using the relationship

$$\Delta F/T = -R \ln K \quad (1)$$

The smoothed values are compared in Table VI with those reported by Rossini and co-authors⁷ from the entropies and heats of combustion. The largest discrepancy appears in the values for 2,2-dimethylbutane.

Since $\Delta F/T$ is related to both ΔH and ΔS through the standard free energy equation and is

also related by equation (1) to the equilibrium constant, it is possible to separate the discrepancies in Table VI and assign them to either errors in the entropy or heat of isomerization or both. From the relation

$$-R \ln K = \Delta H/T - \Delta S \quad (2)$$

the heat of isomerization and entropy of isomerization were evaluated for the conversion of *n*-hexane to its isomers by plotting $\log K$ against $1/T$. The values calculated for the entropy and heat of

 TABLE VII
 COMPARISON OF HEAT OF ISOMERIZATION AND ENTROPY OF ISOMERIZATION DATA FOR THE HEXANES

	$-\Delta H$ cal./mole ^a		$-\Delta S$ e. u. ^a	
	This work	Rossini and co-authors	This work	Rossini and co-authors
<i>n</i> -Hexane	0	0	0	0
2-Methylpentane	-1310	-1710	-0.78	-1.86
3-Methylpentane	-820	-1020	-1.12	-1.59
2,3-Dimethylbutane	-2500	-2530	-6.07	-5.13
2,2-Dimethylbutane	-4620	-4390	-8.93	-6.74

^a Average over the temperature range 25–200°.

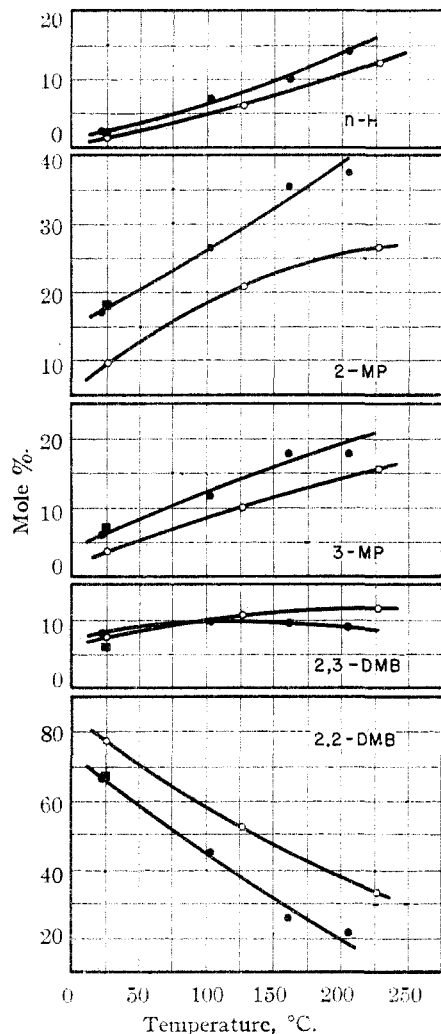


Fig. 3.—●—, Experimental; —○—, calculated from ΔH ; ■, Koch and Richter.

isomerization from the present experimental work and from the calorimetric data of Rossini and co-authors are compared in Table VII. These are the values over the temperature range 25–200° and are directly comparable.

The agreement between the heats of isomerization obtained from the heats of combustion and the present experimental work are quite good. The disagreement in the equilibrium values may be traced largely to discrepancies in the entropies of isomerization. Further work will be necessary to resolve this discrepancy.

Pentanes.—Although this paper deals primarily with hexane equilibria, similar data were obtained simultaneously for the pentanes since the feed contained 37% pentanes. The pentanes were handled in the same fashion as described for the hexanes. The equilibrium values are shown in Table VIII for all temperatures except 21° which was obviously in error. This was due to the loss of a small amount of isopentane when

TABLE VIII
EQUILIBRIUM VALUES FOR THE PENTANES

Temperature, °C.	Mole %			
	102	161	204	
Liquid phase	Isopentane	84.9	74.8	
	<i>n</i> -Pentane	15.1	25.2	
Gas phase	Isopentane	87.2	76.7	71.0
	<i>n</i> -Pentane	12.8	23.3	29.0

washing out the very soluble aluminum bromide used in this experiment before fractionation. These values are compared with the values of Pines, Kvetiuskas, Kassel and Ipatieff⁴ for the gas phase in Fig. 4. The temperature coefficients are widely different and the only agreement is in the neighborhood of 100°.

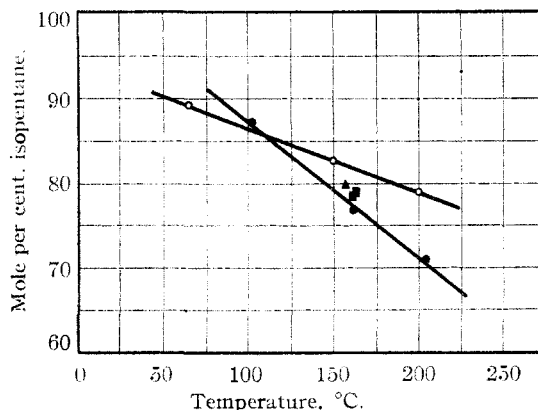


Fig. 4.—●—, Experimental; —○—, Pines *et al.*; ■, check experiments; ▲, no hydrogen.

Since this discrepancy in the pentane equilibria at the higher temperatures might lead one to question the complete establishment of equilibria in the present work, three special experiments were made starting with compositions of pentanes corresponding to the values found by Pines and co-authors and that found in the present work. The results are shown in Table IX. The compositions of the pentane products were accurately determined by mass spectrometer analyses and further checked with infrared analysis. Neopentane was never found as a product of isomerization and is never produced except possibly in minute amounts. Due to the high pressure employed, Experiments 1 and 2, Table IX, were in the liquid phase. These values were converted to the gas phase using the Pines, Kvetiuskas, Kassel and Ipatieff⁴ ratio of K_G°/K_L after slight extrapolation to 160° for more direct comparison. These experiments establish the equilibrium at 78.5% which is in substantial agreement with the value of 77.5% taken from the curve drawn for the values obtained from the present light naphtha work. This agreement establishes that chemical equilibrium had been obtained in the light naphtha reaction system. However, the heat of isomerization and entropy of isomerization calculated from the present experimental values for pentane are

completely in disagreement with those obtained by Rossini and co-authors⁷ as shown in Table X; while the experimental values of Pines, Kvetinskas, Kassel and Ipatieff are in excellent agreement. The reason for this difference is unknown and further work will be necessary to resolve this discrepancy.

TABLE IX
EQUILIBRIUM OF PENTANES AT 160°

Experiment Charge	1	2	3
Mole % isopentane	77.3	82.5	80.6
Mole % <i>n</i> -pentane	22.7	17.5	19.4
H ₂ pressure at room temp.	750	750	0
Benzene inhibitor, %	1.0	1.0	3.0
Reaction time, minutes	65	65	65
Temperature, °C.	161	163	157
Reactor pressure, p. s. i.	1455	1485	495
V/L Ratio at reaction conditions	Liquid	Liquid	0.1
Products			
Mole % decomposition	1.1	2.3	44.6
Mole % based on pentanes			
Liquid phase			
Isopentane	76.9	77.4	78.4
<i>n</i> -Pentane	23.1	22.6	21.5
Vapor phase			
Isopentane	78.3	78.8	79.9
<i>n</i> -Pentane	21.7	21.2	20.1

TABLE X

COMPARISON OF HEAT OF ISOMERIZATION AND ENTROPY OF ISOMERIZATION DATA FOR PENTANES

	ΔH cal./mole	ΔS e. u.
Rossini and co-authors	-1930	-1.32
This paper	-3600	-5.87
Pines and co-authors	-1861	-1.30

Experiment 3, Table IX, was made in the absence of hydrogen pressure to determine its effect

on the pentane equilibrium. There was approximately a 1% increase in isopentane composition indicating no significant effect due to hydrogen pressure. Likewise side reactions to the extent of 44.6% had no important effect on the chemical equilibrium.

Acknowledgment.—The authors are indebted to the numerous members of the Standard Oil Company (Indiana) Research Laboratories who contributed their advice and services and especially to Dr. W. E. Kuentzel for design of the reactor and Mr. J. E. Swearingen for help in calculation of the fugacities.

Summary

1. The experimental equilibria among the isomeric hexanes were determined in the range 21 to 204° using activated aluminum halide catalysts on a 67° end-point light naphtha stock containing both pentanes and hexanes.

2. The results for hexanes agree with the equilibrium values calculated from the heat of combustion and entropy for *n*-hexane and 2,3-dimethylbutane but there is considerable discrepancy for 2,2-dimethylbutane and the methylpentanes. However, there is substantial agreement in the ratio of 2-methylpentane to 3-methylpentane.

3. The experimental equilibria for the pentanes were also determined and show a higher temperature coefficient than that obtained by Pines, Kvetinskas, Kassel and Ipatieff.

4. Hydrogen and extensive side reactions were found not to have any appreciable effect on the equilibria.

WHITING, INDIANA

RECEIVED¹³ SEPTEMBER 27, 1948

(13) Original manuscript received July 8, 1946.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WAYNE UNIVERSITY]

Studies in Stereochemistry. XIV. Reaction of Triethylamine and Quinuclidine with Alkyl Halides; Steric Effects in Displacement Reactions¹

BY HERBERT C. BROWN² AND NELSON R. ELDRÉD³

In previous papers of this series, it has been demonstrated that the stability of addition compounds of the type $R_3N:BR'_3$ invariably decreases as the steric requirements of either R or R' increase. Information gained regarding the effect of structure on the stability of addition compounds should aid in understanding the factors involved in typical displacement reactions.⁴

(1) This paper is based upon a dissertation submitted by Nelson R. Eldred in August, 1946, to the Graduate School of Wayne University in partial fulfillment of the requirements for the degree of Master of Science.

(2) Present address: Department of Chemistry, Purdue University.

(3) Present address: Department of Chemistry, Pennsylvania State College.

(4) Brown and Barbaras, *THIS JOURNAL*, **69**, 1137 (1947).

Consider the reaction of amines with alkyl halides. It is well established that an increase in the steric requirements of the amine increases the steric strain in the addition compound (I) and results in a marked decrease in stability. Similarly, an increase in the steric requirements of the amine should result in a marked increase in steric strain in the activated complex (II) formed from the amine and alkyl halide. In the first instance, a decrease in the heat of dissociation is observed, corresponding in magnitude to the increase in steric strain; in the second, an increase in the energy of activation should be noted, corresponding to the increased strain in the activated complex.

Increase in the steric requirements of the groups